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Guidelines for Surface Water Quality

Vol. 1 Inorganic Chemical Substances

SILVER

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Abstract

A literature survey was carried out on the toxic effects of silver and silver compounds on human health, aquatic life, plants and livestock. The information is summarized in this publication. From it, maximum silver concentrations in water at which toxic effects will not appear are recommended.

Résumé

On a effectué une étude de la documentation portant sur les effets toxiques de l'argent et de composés de l'argent sur les humains, les organismes aquatiques, les plantes et le bétail. Ces données sont résumées dans cette publication. En se basant sur ces données, on propose des valeurs des concentrations maximales d'argent dans l'eau auxquelles on n'observe pas d'effets toxiques.

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RECOMMENDED WATER QUALITY OBJECTIVES FOR SILVER

Uses	Recommended objectives (as total silver)
Raw public water supply	0.05 mg/L for water supplies without treatment or with simple filtration. 0.2 mg/L for water supplies treated by chemical processes.
Aquatic life and wildlife	
Aquatic life	0.0001 mg/L* until further information is available.
Wildlife	No recommended limit owing to insufficient information.
Agricultural water supply	
Livestock watering	No recommended limit owing to insufficient information.
Irrigation	No recommended limit owing to insufficient information.
Recreation and aesthetics	
Recreation	0.05 mg/L
Aesthetics	No recommended limit.
Industrial water supplies	
Food processing	0.05 mg/L for water supplies with no treatment or simple filtration. 0.2 mg/L for water supplies treated by chemical processes.

* Discussed in text in µg/L.

Guidelines for Surface Water Quality
Vol. 1. Inorganic Chemical Substances. Silver

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SOURCES, OCCURRENCE AND FORM

Natural Distribution of Silver

Silver is among the less common but widely distributed elements in the earth's crust. Its average crustal abundance has been estimated at 0.07 mg/kg, ranking it 69th of the 88 elements listed by Taylor (1964). Silver is thus less common than metals such as cadmium and mercury, but more abundant than selenium, gold or platinum. In igneous-type rocks the average silver content varies from 0.04 (granite) to 0.12 mg/kg (gabbro, diabase), while in sedimentary rocks the average silver content ranges from 0.05 (anhydrite, gypsum) to 0.10 mg/kg (normal shale) (MRI 1975, p. 12). Deep-sea sediments contain an estimated 0.11 mg/kg silver (Turekian and Wedepohl 1961).

Silver occurs very rarely as native silver in silver deposits and is usually associated with other metals, for example, copper, zinc, iron and antimony (Thompson 1973; MRI 1975, p. 11ff). In normal soils the silver content ranges from less than 0.1 to 5 mg/kg, with an average concentration of 0.3 mg/kg silver. Near lead-zinc-silver deposits the silver content of most soils is enriched, with values commonly reaching 10 mg/kg or higher (Boyle 1968, p. 61ff). Soil samples taken during drilling to study possible groundwater contamination from sludge land filling and piling, at a North Toronto Sewage Treatment Plant and on neighbouring Canadian National Railway property, were found to contain from 0.5 to 4 mg/kg silver (Van Loon 1975).

Silver concentrations in air at locations near industrial sources ranged from 0.17 to 7.0 ng/m^3 (0.14 to 5.8 ng/kg) (MRI 1975, p. 12). The background concentration of silver in air has been estimated at <0.1 ng/m^3 (Mulvey 1978).

Silver in Water

Estimates for the concentration of silver in seawater vary from 0.15 to 2.9 µg/L (Bowen 1966; Thompson 1973; Boyle 1968, p. 77ff; MRI 1975, p. 13). There is a general tendency for the silver concentration to increase with depth in areas of high organic productivity (Boyle 1968, p. 79).

Surface waters in non-industrialized areas contained an estimated average of 0.2 µg/L silver (Boyle 1968, p. 74ff), whereas in industrialized areas the silver concentration of surface waters reached 38 µg/L (MRI 1975, p. 13ff). Acid waters tend to contain more silver than neutral or alkaline waters. Chloride, sulphate, bicarbonate and organic waters and waters containing an abundance of dissolved iron and manganese also seem to be enriched with silver. Silver in water is often accompanied by Cu, Zn, Cd, V and U, and less commonly by other metals, such as Ba, Sn, As, Pb, Ni and Co. Waters passing over gold-silver and polymetallic deposits tend to have silver concentrations 10 to 100 times greater than normal waters (Boyle 1968, p. 75). Measurements for silver recorded in NAQUADAT indicated that the silver concentration of 90% of the water samples was below the detection limit, which ranged from 4 to 10 µg/L (Environment Canada 1978).

Silver is present in precipitation. Rainfall samples from a remote area of Ontario, the Perch Lake basin, contained 0.0028 to 0.03 µg/L silver, and precipitation in Germany contained 0.07 to 9 µg/L (Merritt 1976). A table compiled by Mulvey (1978) shows a range for silver concentration in various types of precipitation (rain, snow, hail) at various locations in the United States of 0 to 1.2 µg/L.

As would be expected, cloud seeding with silver iodide (AgI) increases the concentration of silver in rain. In Alberta, for example, the concentration of silver in rainfall during two storms that had been seeded with 240 g AgI was found to be 0.046 and 0.062 µg/L, well above the normal concentration of 0.005 µg/L of silver in rainfall in the area. The silver concentration in the rain samples from the two "seeded" storms was very dependent on the time of sample collection, reaching a maximum after 56 and 70 min, respectively (Warburton 1973). Another study (Zacharuk and Erb 1977), also carried out in Alberta, showed the mean concentration of silver from unseeded storms to be approximately 0.0025 µg/L. Silver concentrations above 0.006 µg/L were considered to

indicate silver contamination from cloud seeding. Such contamination was found to affect a very large area, with positive silver identifications made as far as 102 km from the point of seeding.

Stream sediments near mineralized zones have been found to be enriched with silver, averaging 0.93 mg/kg, compared with an average of about 0.14 mg/kg in normal sediments (Boyle 1968, p. 68). Analyses of suspended sediments from a number of streams in the United States showed a range of 0.3 to 15 mg/kg silver (Turekian and Scott 1967). The highest values were found in the Susquehanna River of Pennsylvania, which flows through industrialized areas.

The soil and sediment enrichment of silver is accompanied by parallel enrichments of Ba, Sr, Pb, Zn, As and Sb. Where manganese dioxide occurred, the content of silver reached a maximum, indicating the strong adsorption capacity of manganese soils for the element (Boyle 1968, p. 68). McDuffie *et al.* (1976) found that the concentration of silver, and that of other trace metals (Cd, Cu, Hg, etc.), increased as the particle size decreased.

Production and Uses of Silver

The production of silver in Canada in 1974 and 1975 was 1332 and 1216 tonnes, respectively. Of this amount 845 and 902 tonnes, respectively, were refined silver, and the rest was silver ores or concentrates. In 1974 Canada was the largest producer of silver, with 14.4% of the world's production of 9216 tonnes, followed closely by the USSR, Peru, Mexico and the United States. In Canada, Ontario is the largest producer with approximately 40% of the nation's silver production, followed by the Yukon Territory and British Columbia with about 15% each, New Brunswick with approximately 11% and Quebec with about 8% (George 1976). Approximately 90% of the annual world production of silver is obtained as a by-product of lead-zinc, copper and gold mining. The remainder comes from deposits which are exploited for silver (Boyle 1968, p. 227).

The Canadian consumption of silver was 332 tonnes in 1974 and 330 tonnes in 1975, representing 25 and 27% of the respective productions. These percentages are rather misleading, however, as Canada is both a large exporter and importer of silver. In 1974, for example, Canada exported 1267 tonnes, 603 tonnes as ore and concentrates and 664 tonnes as refined silver. This represented almost the entire production of silver for the year, but at the same time, Canada was importing 910 tonnes of silver, most of it from the United States and the United Kingdom. In 1975 the imports decreased considerably to 421 tonnes (George 1976).

The United States is the world's largest consumer of silver. Its consumption was 5537 tonnes in 1974 and 4989 tonnes in 1975. The largest portion of this consumption (29.2% in 1975) was used for photographic materials. Other major uses of silver are in the manufacture of sterling and plated ware, jewelry, coins and medallions, electrical and electronic products such as batteries, contacts and conductors, brazing alloys and solders, catalysts, mirrors, and dental and medical supplies.

Between 600 and 700 kg of silver iodide were used in cloud seeding over western Canada in 1977 (A.J.Chisholm, Atmospheric Environment Service, personal communication).

Pathways for Entering the Environment

Natural processes, such as weathering and volcanic activity, release silver to the environment. Data quoted by Boyle (1968, p. 77) show that silver has been found in various products of fumarolic and volcanic activity associated with sulphur (sulphides, sulphates), chlorides and ammonia salts. As in the case of other metals, no estimates of the amount released to the environment via this pathway were found in the literature.

Bertine and Goldberg (1971) estimated the amount of silver entering the world's oceans as a result of weathering to be 11 000 tonnes per year.

Various human activities release silver to the environment. The report of the Midwest Research Institute (MRI 1975, pp. 291ff) estimated that in the United States between 1966 and 1972 a yearly average of 1263 tonnes of silver or approximately 25% of the annual consumption, was present in products that might be buried, incinerated, lagooned, or lost directly to water. Of this amount, approximately 10% was estimated to be lost directly to water as unrecycled photographic silver and another 30% to be present in sewage sludge. The other 60% was estimated to be present in combustible refuse and discarded household appliances.

The same report (MRI 1975, p. 335) also quoted estimates of silver released to the atmosphere in the United States. The total amount was estimated to be 327 tonnes, of which the iron and steel industry contributed 54%, the cement industry 29% and the burning of coal 12%.

The concentration of silver in coal ranges from approximately 0.04 to 2 mg/kg (Demayo *et al.* 1979). The world's consumption of coal in 1974 was approximately 3 billion tonnes. Using an estimated average concentration of 0.1 mg/kg, the amount of silver present in the coal

consumed during 1974 was about 300 tonnes. It has been estimated that only half of the coal production is burned to produce energy, and only 10% of the silver would be released to the atmosphere in the fly ash (Bertine and Goldberg 1971; McMullen 1976).

The concentration of silver in crude oil is much smaller than in coal, only about 0.0001 mg/kg (Bertine and Goldberg 1971), thus the world's production of crude oil in 1976 (2.47 billion tonnes) contained about 0.2 tonnes of silver. Even assuming a 100% release of this silver to the environment, the contribution from this source is still relatively small.

Using the figures cited above, the United States values, and the percentage contributions of the various sectors, it can be calculated that on a global scale the amount of silver entering the environment as a result of human activities could be as high as 2500 tonnes (Klein and Mulvey 1978). This amount, although smaller than the amount entering the environment as a result of the weathering process, is still significant.

As noted, silver also enters the environment through the use of AgI in cloud seeding for weather modification. It has been estimated that this amounts to only 3 tonnes per year or 0.15% of the total amount of silver being released to the environment annually (Klein and Mulvey 1978). Most of the silver falling in precipitation is eventually delivered to streams and lakes by surface runoff or through subsurface layers making little contact with soil colloids. Silver in precipitation falling directly into lakes and streams is, of course, immediately introduced into the aquatic system (Cooper and Jolly 1970).

Freeman (1976) studied the seasonal fluctuation of silver in various components of Buckeye Lake, a small alpine lake in the southern Gore Range, Lake County, Colorado. In the summer, silver apparently becomes associated with the terrestrial and aquatic communities and its concentration in soil increases, the net result being low concentrations of silver in the aqueous medium. At the end of the growing season large-scale die-offs and chemical reversals in the soil lead to higher concentrations of silver in the surface and groundwater. Similarly, die-offs in the lake lead to higher concentrations of silver in the sediments, and these levels remain high under the ice during the winter as a result of the accumulated biological fallout of the preceding autumn. Redox reactions, with iron, for example, are also likely to contribute to increased silver levels in the sediments. Silver levels in plankton are low during winter. In the spring, surface and groundwaters contain about the same levels of silver as were present in the preceding fall at freeze-up. As the lake thaws, the biological activity both on land and in the lake re-initiates the cycle, silver again becoming associated with the biotic communities.

Forms of Silver

Silver exists in the oxidation states of 0, +1, and +2. The most common are the metal (0 oxidation) and the argentous ion (+1 oxidation). The argentic ion (+2 oxidation) is obtained by the oxidation of acidified solutions of argentous salts with persulphate ion, fluorine or ozone. Once formed, Ag(II) solutions are fairly stable in acidified aqueous solutions, the most stable being those in phosphoric acid, probably due to the stability of the Ag(II)-phosphate complexes which are formed. The reduction to monovalent silver takes place slowly in all cases (Thompson 1973).

In natural waters silver occurs in the +1 oxidation state as sulphate, bicarbonate or nitrate. In waters containing high concentrations of NaCl or KCl, complexes of the form $Na(AgCl_2)$ occur. This is the form in which silver is probably present in seawater. It has been suggested that silver is supplied to the oceans mainly (up to 90%) as dissolved species (Kharkar *et al.* 1968). In areas of high biological activity, such as in or about reef complexes in the oceans, $[Ag(S_2O_3)_2]^{3-}$ is probably stable only at low temperatures for short periods of time in near-surface environments. This complex is soluble in alkaline and neutral solutions but is decomposed to S, Ag_2S, and some Ag_2SO_4 in acidic solutions.

Silver thiosulphate complexes, found in waste photographic solutions, are the main form in which the approximately 500 tonnes of silver enters the environment each year in the United States alone. It has been estimated that 75% of these silver thiosulphate complexes are eventually trapped in sewage sludge (MRI 1975, p. 402).

In water or vapours containing high concentrations of H_2S or S^{2-}, complex sulphide or polysulphide ions, or hydrosulphides, might form. Silver may also be dissolved as double complexes of sulphur, arsenic, antimony, tellurium and selenium (Boyle 1968, p. 80).

Silver may exist in water in colloidal form (as compounds such as AgCl, Ag_2S, Ag_2Se and Ag_3AsS_3), as an integral part of or adsorbed onto various humic complexes, or in a dissolved form (as simple organic compounds, e.g. acetate and tartrate, or more complex ones) (Boyle 1968, p. 81).

In acidic solutions the argentous ion is soluble and mobile, but as the acidity of solutions is reduced, silver tends to precipitate. At a pH of 7.5 to 8.0 silver hydrolyzes from aqueous solution as the oxide or basic salts. Silver is

relatively insoluble in alkaline solutions unless ammonia or some other complexing agent is present. The precipitation of silver from natural waters is also a function of the other ions present. For example, silver can be precipitated as a halide when silver-bearing waters mix with water containing Cl^-, Br^- or I^- ions, as Ag_2S when silver-containing waters come into contact with H_2S or S^{2-}, and as silver phosphate, chromate, or arsenate when PO_4^{3-}, CrO_4^{2-}, or AsO_4^{3-}, respectively, are present. These and other possible processes by which silver can precipitate from natural waters or vapours are discussed by Boyle (1968, pp. 81ff).

Silver is also present in the aquatic environment adsorbed onto plankton and various colloids, and in the tissues of microorganisms, etc. (MRI 1975, p. 402; Boyle 1968, p. 83).

Theoretical equilibrium calculations (Morel *et al.* 1973; Hem 1977) have shown that in aqueous solution the predominant silver forms are Ag+ and AgCl. At a concentration of 1 µg/L of silver, 60% was present as Ag+ and the rest as AgCl. The introduction of a series of organic complexing agents (NTA, citrate, glycine, and cysteine) into the equilibrium calculations changed the results very little.

Model calculations for an estuarine environment have shown that with a dissolved silver concentration of 0.04 µg/L and an H_2S+HS^- concentration of 0.01 µg/L, at the river end AgHS was by far the most important species present, followed by Ag^+ and AgCl. At the marine end, the activity of $AgCl_2^-$ was the highest, followed closely by that of AgHS, $AgCl_3^{2-}$ and $AgCl_4^{3-}$. In marine waters, $AgCl_2^-$ and $AgCl_3^{2-}$ complexes are the most important species (Jenne *et al.* 1978).

Studies with radiosilver released from nuclear power stations have shown that in a freshwater environment and at a slightly alkaline pH (~8.0) 50% or more of the silver precipitated. As a consequence of this, within 48 h 80% of the radiosilver had been adsorbed onto the sediments from the freshwater medium. In sea or estuarine waters, because of the presence of a high concentration of chloride ions, silver is rapidly desorbed (70% in 24 h) and remains in solution (Fukai and Murray 1973; Murray and Murray 1973).

RATIONALE

Raw Public Water Supplies

Silver in the Human Body

Silver has no known function in the human body and is considered to be a contaminant when found in human tissues. Possible intake routes are the respiratory and gastrointestinal tracts, the mucous membranes and broken skin. According to data quoted by Klein (1978e) 10% of the ingested silver is absorbed, but only 4% is then retained in the tissues. Within the body, silver is transported mainly via the blood plasma, probably as silver chloride or albuminate, and is deposited in all organs. The primary sites of silver deposition in persons who have never taken silver therapeutically are the liver, skin, pancreas, adrenals, kidney, brain, blood vessel walls, spleen and testes. The tissue content and distribution depend on the intake route, the amount administered, and its chemical form (MRI 1975, p. 356). On a wet weight basis the silver concentration in various human tissues (brain, kidney, lymph nodes, lung, muscle, testes, ovary) ranged between 0.001 and 0.004 mg/kg. The rib bone had a much higher concentration, 101 mg/kg, and was therefore outside this range (Klein 1978e). On a dry weight or ash basis some values for normal tissues were: spleen, 2.68 mg/kg (dry basis); liver, 0.70 to 1.70 mg/kg (ash); kidney, 0.36 mg/kg (dry basis); brain, 0.5 to 1.7 mg/kg (ash); and skin, 1.3 mg/kg (ash) (MRI 1975, p. 54ff). Silver apparently accumulated in the body with age even when none had been administered intentionally. Creason *et al.* (1976) found that silver levels in the placenta (mean: 0.005 mg/kg) and blood samples from the umbilical cord (mean: 0.005 mg/L) were equal to or slightly higher than levels in the maternal blood samples, which averaged 0.004 mg/L.

The average human intake of silver from the diet has been estimated at up to 0.088 mg/day and the excretion via the feces at approximately 0.06 mg/day (Kehoe *et al.* 1940). Animal experiments with radiosilver have shown that mice and rats eliminated 99.61 and 98.35% respectively, two days after oral administration of silver. The elimination was slightly less for other animals: monkey, 94.35% and dog, 90.38% (Furchner *et al.* 1968). Except in the dog, whole-body retention was less than 1% of the initial dose after one week. Silver was excreted mainly through the gut, and retention in all tissues except the brain and spleen resembled whole-body retention. Very little silver, if any, was eliminated via the urine, but administration of Ca-EDTA increased the urinary excretion of silver. The average silver content of the human body in the United States has been estimated at 0.05 mg/kg (wet basis) (MRI 1975, p. 357).

The Toxicity of Silver

Silver is one of the metals with very high "oligodynamic" activity, being second only to copper in many circumstances. The term "oligodynamic activity" refers to solutions with germicidal properties in which the metal ion concentration is many orders of magnitude below that which would be lethal to mammals. To primitive life forms, silver is as toxic as the most powerful chemical

disinfectant, and this, coupled with its relatively low toxicity to higher forms of life, gives it great potential as a disinfectant. The concentration required to sterilize water contaminated with non-sporulating bacteria has been quoted at 0.04 to 0.2 mg/L, while water containing 0.25 mg/L showed a very strong oligodynamic activity towards various gram-positive and gram-negative microorganisms. This low metal ion concentration singled out silver from other oligodynamically active metals, since silver metal itself or one of its insoluble salts can be maintained in contact with the sterile liquid indefinitely without the buildup of a silver ion concentration lethal to higher organisms (Thompson 1973, p. 80). The Russians believe that silver is the safest and longest lasting method for converting polluted waste into potable water on board space stations and spaceships (MRI 1975, p. 361).

The biological action of silver apparently involves reversible chemical bonding with enzymes and other active molecules at the cell surface. For silver to be toxic in low doses, the ionic form of the metal must come into direct contact with metabolically active sites, such as the cell membranes of microorganisms. The lipid phase of the cell membrane appears to play an important role in the adsorption of silver ions by living cells. Binding of -SH groups seems to be the principal mechanism by which silver ions inhibit enzyme activity (Cooper and Jolly 1970). Interference with the active transport across membranes and the *in vitro* metabolism of cyclic adenosine monophosphate have also been reported even though sulphydryl groups might not be present. Another major site of biochemical interaction is the cell DNA, to which the silver binds reversibly at several reactive groups such as bases, riboses and phosphates. The effects of silver on a series of other biochemical processes have been summarized by Klein (1978a,b).

Toxicity of Silver to Humans

Sollmann (1957) observed that ingestion of silver nitrate in doses of 0.01 to 1.0 g produced no symptoms, but that 2 to 30 g caused death within a few hours to a few days. Silver nitrate taken orally caused necrosis of the gastrointestinal tract. In the body, silver is precipitated by chloride ion or protein. Experimental evidence has shown that radiosilver is retained mainly by the reticuloendothelial system (MRI 1975, p. 355).

Generalized argyria, localized argyria, and argyrosis (argyria of the eye, unless otherwise stated) are the most common effects of chronic exposure to silver. Argyria occurred almost exclusively among silver nitrate makers and in some workers involved in mirror plating, silver mixing, photographic plate making and glass bead silvering, but it can also occur as a result of medicinal applications of silver. Generalized argyria is characterized by a slate-gray colouring of the skin and hair caused by deposition of silver in the tissues. Other symptoms include a silver colouration of the fingernails, a blue halo around the cornea and in the conjunctiva, disturbance of dark adaptation, and turbidity of the anterior lens capsule. Other deposition sites are the skin, glomeruli of the kidney, choroid plexus, mesenteric glands and the thyroid. Possible deposition sites are bone marrow, pancreas, liver, spleen, testes and ovaries. Argyria may also affect the respiratory system (MRI 1975, p. 357).

Data quoted by Green and Bunyan (1969) showed that 130 mg/L of silver in the drinking water or food produced liver necrosis in rats. This toxic effect was prevented by 0.05 mg/L selenium. Apparently silver produced the same type of hepatic degeneration as selenium deficiency.

Recommended Objective for Silver in Raw Public Water Supplies

Silver is one of the non-essential elements for human health. Although silver is very toxic to lower forms of life in very low concentrations, it becomes toxic to humans only when ingested in quantities in the order of a gram per day.

Chemical treatment by the lime (CaO) coagulation-settling process at a pH of 11 removed 97.0% of the silver. The effluent had a concentration of <0.0046 mg/L. Simple sand filtration of this secondary effluent to which 0.050 mg/L silver had been added to give a composite silver concentration of <0.0546 mg/L removed 11.6% of the silver. Subsequent activated carbon treatment increased the removal efficiency to 97.1%, then cation exchange to 98.8% and finally anion exchange to 99.4% (Linstedt *et al.* 1971). Similar results were quoted by Cohen (1977). A lime precipitation-activated carbon treatment removed 98% of the silver, leaving a residual concentration of 0.010 mg/L. Ferric chloride-activated carbon removed 99.1% of the silver, and alum-activated carbon removed 99.2%. In the last two processes the residual silver concentration was 0.005 mg/L. A secondary effluent from Orange County, Florida, had a silver concentration ranging up to 0.01 mg/L. Further treatment of this effluent had little effect on the silver concentration (Argo and Culp 1972).

The *Guidelines for Canadian Drinking Water Quality* (HWC 1978) recommended a maximum acceptable concentration of 0.05 mg Ag/L. The same limit is allowed by the U.S. Public Health Service. If a person

drinks 2 litres of water per day with a concentration of 0.05 mg/L, and no silver is eliminated from the body, it would take 27 years to ingest 1 gram of silver, the toxic level of this metal for humans.

The Australian water quality criteria (Hart 1974, p. 51) recommended a limit of 0.05 mg Ag/L for raw domestic water supplies.

A limit of 0.05 mg/L is recommended in this document for water supplies that will be used without treatment or for which treatment consists only of a simple filtration. For waters that are treated by chemical processes, a limit of 0.2 mg/L is recommended.

Aquatic Life and Wildlife

Aquatic Life

Uncontaminated waters contain about 0.2 µg/L silver (Boyle 1968, p. 74). Raw water from Lake Ontario sampled at an intake pipe contained 1.0 µg/L silver (Bard *et al.* 1976). In areas of Canada where mining and smelting are carried on, e.g. Sudbury, contamination by smelting waste containing heavy metals including nickel, copper, and silver occurs. The concentration of silver in waters of these areas ranges from 1.0 to 37 µg/L (Stokes *et al.* 1973).

Bioaccumulation of Silver

Algae (*Scenedesmus* sp.) and *Daphnia magna* (microcrustacean) absorbed silver from the water. The concentration factor for *Daphnia* was lower than for the algae, 26 compared with 96 (water of 500 µg/L), and this gives an indication of the difference in magnitude which could occur under natural conditions (Terhaar *et al.* 1977). *Lemna minor* had a silver concentration of 33 µg/L (dry weight) from water containing 0.4 µg Ag/L, which is a non-toxic level, (Hutchinson and Czyrska 1975).

Cowgill (1973) studied the concentration of silver in water lilies and the aphids (green fly) that fed on them. The aquatic plants contained from 60 to 2300 µg/kg (average, 500 µg/kg) and the aphids averaged 420 µg/kg. The plants showed only a 2-fold increase in silver levels over levels in the substrate. The silver concentration in water that left the lake system was 0.012 µg/L. It was thought that silver could not diffuse from the mud in the presence of FeS, unlike mercury, which could form stable volatile methyl compounds.

Daphnia feeding on *Euglena* or mixed freshwater algae did not bioconcentrate silver from the algae, which had concentrations of silver of 7.5-fold over levels of silver in the water (Cowgill and Burns 1975).

Fish (*Pimephales promelas*, fathead minnow) concentrated silver from the water but not to such an extent as *Daphnia* sp. It was thought that fish did not accumulate silver via the *Daphnia* (food web). The aquatic organisms used in the tests accumulated silver from the water, but those at higher trophic levels contained less per unit weight and there was no evidence of biomagnification through the food web. The mechanism of bioaccumulation, absorption or adsorption was not studied or fully explained (Terhaar *et al.* 1977). The absence of biomagnification was also discussed by Bard *et al.* (1976). The level of silver in fish from the St. Lawrence River ranged from 10 to 30 µg/kg (fresh weight), and the level of silver in the river water was 1 to 6 µg/L, giving a concentration factor in the neighbourhood of 13. It was not thought that this level of silver would be a hazard to fish consumers (Tong *et al.* 1972). Concentrations of silver in Lake Michigan fish muscle (wet weight) ranged from 28 µg/kg in yellow perch to 44 µg/kg in brown trout. Whole fish analyses gave 34 µg/kg in alewife and 39 µg/kg in rainbow smelt (Copeland *et al.* 1973).

A study conducted in Colorado showed that silver concentrations in chironomid and caddisfly larvae closely followed trends in sediment concentrations in 1974, but the correlations were not so close in 1973. The ecosystem used in the study was simple, and sampling may have affected the natural balance in biomass distribution. Mean silver concentrations in chironomids were 2600 µg/kg in 1973 and 560 µg/kg in 1974; in caddisfly larvae, 400 µg/kg in 1973 and 120 µg/kg in 1974. Mean sediment levels were 510 µg/kg in 1973 and 290 µg/kg in 1974; physical factors were thought to be responsible for the lower silver levels in the abiotic environment in 1974. Plankton concentrated silver from the water. Lake water carried up to 1 µg Ag/L, and the substrate and organisms concentrated silver up to 10 000 µg/kg. Magnification of silver through the food web was not a problem. Cutthroat trout carried silver levels of 3690, 1810 and 290 µg/kg in the bone, liver and muscle, respectively (Freeman 1975).

Toxicity of Silver to Algae, Bacteria and Microinvertebrates

The effect on aquatic organisms of metals involved in the contamination of the Sudbury area lakes was investigated using test solutions of several metals both alone and in various combinations. Strains of two species of algae from the lakes and from a laboratory culture were used to study the effects of silver on growth. *Scenedesmus* sp. from the laboratory grew at 50 µg Ag/L, but growth was completely inhibited at 100 µg/L. Growth of the lake strain was not completely inhibited until the concentration of silver reached 200 µg/L. Growth of the labo-

ratory strain of *Chlorella* was inhibited at 30 µg/L, but the lake strain grew at 50 µg/L and was not completely inhibited until the silver concentration reached 100 µg/L. The character of the responses of the lake and laboratory strains to the presence of silver was different. A complete cutoff occurred with the laboratory strain, but growth of the lake strain gradually slowed as the level of silver increased. The lake algae were more tolerant to silver and also exhibited this tolerance with other heavy metals (Stokes *et al*. 1973).

The growth of *Chlorella vulgaris* was initially retarded at 10 µg Ag/L and was completely inhibited by 60 µg/L. *Chlorella* sp. isolated from lakes containing high levels of nickel were tolerant to nickel and also exhibited a tolerance to silver even though silver was not present in significant concentrations in the lakes (1 to 37 µg Ag/L) but this phenomenon could not be explained (Hutchinson and Stokes 1975). Silver was shown to be the most toxic of nine metals tested (Cd, Cu, Hg, Se, Ni, Co, Ba, Pb) (Hutchinson 1973). The International Joint Commission (IJC 1977) quoted research giving similar levels for effects of silver on algae. Similar magnitudes of toxicity were shown by Bringmann and Kühn (1959). Lethal levels of silver (as $AgNO_3$) were 40, 50 and 30 µg/L for *Escherichia coli*, *Scenedesmus quadricauda* and *Daphnia magna*, respectively. Precise comparisons cannot be made between experiments, as the different experimental conditions would have some effect on toxicity.

The concentrations of silver (as $AgNO_3$) causing the onset of inhibition of cell multiplication (toxicity threshold) for the blue-green alga *Microcystis aeruginosa* and the green alga *Scenedesmus quadricauda* were 0.7 and 9.5 µg Ag/L respectively. Bidistilled water and stock nutrient solution were used for the test and control cultures (Bringmann and Kühn 1978).

Silver was less toxic to *Lemna valdiviana* (duckweed) and *Salvinia natans* (floating fern) than to the green algae *Chlorella* sp. and *Scenedesmus* sp. There was no inhibitory effect on the growth at 50 µg/L, but there was inhibition at 500 µg Ag/L (Hutchinson and Czyrska 1975).

No chemical evidence has been presented to indicate that silver can be transformed into hazardous and biologically available compounds comparable to methylmercury. Ionic silver is more toxic to aquatic organisms than compounds of silver. Some compounds, such as thiosulphate-complexed silver, break down to silver sulphide, which is much less toxic to aquatic organisms than the silver ion. Silver thiosulphate, a component of the photographic industry effluent and insoluble Ag_2S were shown to have no effect on activated sludge at levels of 100 000 µg/L, but much smaller concentrations of freely dissociated $AgNO_3$ (10 000 µg/L) and of AgCl (10 000 µg/L) caused an 84% and a 43% inhibition of oxygen uptake, respectively (Bard *et al*. 1976).

Mowat (1976) studied the toxicity of a number of metals by measuring changes in biochemical oxygen demand in the standard BOD_5 test using inocula of 5% raw wastewater composites. The BOD test was run at the standard pH 7.2. The essential minerals in the dilution water affected the solubilities of many of the metals, for example, some of the Ag^+ was precipitated by the Cl^- present from $CaCl_2$ and $FeCl_3$. In 5 days of exposure to silver, there was a 25 to 38% uptake of dissolved oxygen at the 1000 µg Ag/L level (average 31%); 31 to 50% uptake (average 40%) at 500 µg Ag/L, and 42 to 77% uptake (average 53%) at 100 µg Ag/L, compared with controls where the amount of dissolved oxygen taken up was over 90% of the available oxygen.

Freshwater bacteria were shown to be sensitive to silver; community numbers were not affected, but the heterotrophic activity was affected by 0.1 and 0.01 µg/L silver. Further research is needed into the study of heterotrophic microbes in natural waters and the effects of pollutants on them (Albright *et al*. 1972).

Klein and Giangiordano (1976) demonstrated that silver (5, 10, 100 µg/L) caused an increase in growth delays at low temperatures in populations of *E. coli* and *Hyphomicrobium*. If the cells, inhibited by the presence of silver, were transferred to a more suitable temperature (9° to 16° C), the silver ion effect was neutralized and the survivors grew normally.

Five bacterial genera studied by Annear and Mee (1976) showed inhibition at concentrations of 3.6 to 11.4 µg Ag/mL (as silver nitrate), but at higher concentrations (15.2 to 26.7 µg Ag/mL) growth was observed. This is opposite to what would have been expected.

The main biological effects of the silver ion on *Pseudomonas aeruginosa* were caused by the interaction with DNA (deoxyribonucleic acid). Inhibition of growth started at a concentration of approximately 0.32 µg Ag/L (0.003 µmol/L as silver sulfadiazine) and it was total at a concentration of 5.4 µg Ag/L. Cell death occurred at 21.6 µg Ag/L. The silver ion binding to DNA was both chemically and biologically reversible (Modak and Fox 1973).

Many instances of the acquisition of resistance to silver by microorganisms are cited by Klein (1978b). In the available work looked at by Klein, the evolution of heavy metal-resistant enzymes was thought to be restricted to microorganisms.

The effect of silver iodide, which is used in cloud seeding, on microorganisms has been studied by a number of authors (quoted in Klein 1978b), but relatively high concentrations had to be used to obtain toxic effects.

Bacterial and fungal spores appear to be more resistant to the presence of silver than the vegetative forms, and yeasts showed greater resistance than bacteria (Klein 1978b).

Rotifers are a major part of some fish diets and the effects of heavy metals on them have been studied by Buikema *et al.* (1974). The 96-h EC_{50} (the concentration of silver which affected 50% of the rotifers after a specified length of time) for *Philodina acuticornis* in soft water (17 mg/L as $CaCO_3$) was 1400 to 1700 µg Ag/L (as $AgNO_3$).

Toxicity of Silver to Insects

The immature stages of *Ephemerella grandis* (mayfly) and *Pteronarcys californica* (stonefly) were less tolerant of silver than fish (rainbow trout). Aquatic insects are usually less sensitive to heavy metals than fish, but silver is an exception. The 14-d TL_{50} for mayfly was less than 1 µg Ag/L and for stonefly between 4 and 9 µg Ag/L. The average accumulation of silver in the two organisms was 195 times the concentration of silver in the water for mayfly, and 113 for stonefly (Nehring 1976). The 7-d LC_{50} for immature stoneflies (*Pteronarcys californica*) lay below 4 µg/L. *Ephemerella grandis* (mayfly) is less tolerant than *P. californica* and the lowest concentration tested (9 µg/L) killed 96% of the mayflies in 240 h (Goettl *et al.* 1976?).

Toxicity of Silver to Fish

The hardness of water has been shown to affect the toxicity of some heavy metals, e.g. zinc and copper, but silver does not appear to be affected as much. The 96-h LC_{50} for rainbow trout (*Salmo gairdneri*) was 8.1 µg/L at a hardness of 26 mg/L as $CaCO_3$ and 13 µg/L at a hardness of 350 mg/L as $CaCO_3$. Developing eggs were exposed to various concentrations of silver nitrate and the level of no effect lay between 0.09 and 0.17 µg Ag/L. Concentrations above 1.0 µg/L caused eyed eggs to hatch before development had been completed, and the fry died very shortly after hatching. Silver iodide was more toxic than silver nitrate; the level of no effect lay between 0.03 and 0.07 µg Ag/L (Goettl *et al.* 1976?). Davies (1976) recommended a concentration between 0.07 and 0.13 µg/L as being "safe". After a one-year exposure to various concentrations of silver the mortality of rainbow trout fry after swim-up decreased from 38% at 0.50 µg Ag/L to 18% at 0.13 µg/L and 3% mortality at 0.07 µg/L (there was no control mortality). The 96-h LC_{50} for *Cyprinus carpio* (carp) was 3.8 µg/L $AgNO_3$ at a hardness of 118 mg/L as $CaCO_3$ (Rao *et al.* 1975). The irregular swimming noted by Coleman and Cearley (1974) was also recorded.

Largemouth bass (*Micropterus salmoides* Lacépède) were more susceptible to silver, as silver nitrate, than bluegill (*Lepomis macrochirus* Rafinesque) and all were dead at a level of 70 µg/L in 24 h. Bluegill tolerated this level and survived for the period of the study, 6 months. The survival of both species in 7 and 0.9 µg Ag/L was comparable to the controls over 6 months. Body accumulations in bass exposed to 7 µg Ag/L were highest in the gills, approximately 200-fold; the remainder of the body and internal organs contained levels of silver 9-fold to 12-fold, respectively, greater than the control fish. By 2 months, an equilibrium had developed between the concentration of silver in the tissues of the bass and the water. The overall concentration of silver was higher in the internal organs (600 µg/kg) than in the gills (370 µg/kg) or the rest of the body (17 µg/kg). Possible causes of death were discussed; the gills did not secrete excessive amounts of mucus but they were a brighter red than those of the controls and there may have been an effect on the respiratory system. An effect on the nervous system may have been present because of tremors and erratic swimming behaviour, but these symptoms can also occur in respiratory failure. The effect of silver on the growth rate was not significant at the levels tested, but other physiological functions such as reproduction and egg viability were not tested (Coleman and Cearley 1974).

A 13-month study in which silver iodide was used (with no chelating agent added) indicated that the MATC (maximum acceptable toxicant concentration) for eyed rainbow trout eggs lay between 0.03 and 0.06 µg/L. Fish from eggs exposed at an earlier developmental stage tolerated higher concentrations of silver (0.18 to 0.40 µg/L) and this was probably due to embryonic acclimation to silver. It was not thought that silver iodide (from cloud seeding) would pose a serious threat to aquatic life because of its low solubility (Davies and Goettl 1978).

Silver inhibits the activity of enzymes, probably by combining with the electron-rich functional groups, particularly sulphydryl groups. Silver was similar in toxicity to mercury in the *in vitro* experiments conducted on the enzymes glutamic oxalacetic transaminase (GOT) and lactic dehydrogenase (LDH) obtained from white sucker (*Catostomus commersoni*) blood plasma. Of the metals tested, GOT was most sensitive to silver, and complete

inhibition was caused by a concentration of 50 000 µg/L. LDH was not as sensitive to silver (Christensen 1971/72). The results of this study cannot be directly applied to the natural situation, as the silver in rivers and lakes may not reach the enzymes within the cells, but the study illustrated that silver is very toxic compared with a number of heavy metals.

Jackim *et al.* (1970) studied the activity of five liver enzymes from the estuarine killifish (*Fundulus heteroclitus*) after *in vivo* exposure to toxic metals approximating the 96-h LC_{50} concentration (Cu, Hg, Pb, Cd, Ag, Be). *In vitro* experiments were also conducted on the enzymes for comparison. Silver did not affect all the enzymes to the same degree; liver acid phosphatase activity was not significantly affected by silver *in vivo* even though there was a 50% inhibition of activity by 10^{-4} mol/L (10 800 µg/L) *in vitro*. Other metals were more toxic than silver to some of the other enzymes. Mercury and silver were the most potent inhibiters of catalase exposed *in vitro*, and fish exposed to the 96-h LC_{50} (approximately 40 µg/L) exhibited a decrease in liver catalase activity. Differences in reactions between *in vivo* and *in vitro* exposure emphasize the caution that has to be exercised in interpreting *in vitro* studies and applying the results to natural ecosystems, as different chemical mechanisms may be involved under the two conditions. Jackim (1973) showed that 20 µg Ag/L increased the activity of hepatic δ-aminolevulinic acid dehydratase (ALA-D) in fish exposed to sublethal levels.

Wildlife

No references have been found in the literature which discuss toxic effects of silver on wildlife.

Recommended Objectives for Aquatic Organisms and Wildlife

Levels of "no effect" for trout lay between 0.09 and 0.17 µg/L (developing eggs); 0.03 and 0.07 µg/L (18 months) and 0.07 and 0.13 µg Ag/L. Acute toxicity for insects was evident at silver concentrations of <1 µg/L for mayfly and between 4 and 9 µg/L for stonefly.

Cell multiplication of *Scenedesmus* was inhibited by 0.7 µg/L and the heterotrophic activity of freshwater bacteria was affected by 0.1 and 0.01 µg/L. Silver was shown to be the most toxic metal of nine metals tested using algae.

Many silver compounds have very low solubilities in water, but silver has been shown to be toxic at concentrations below the solubility values. Toxicity data using soluble silver salts have indicated that levels of 0.04 µg/L should be safe. Silver will precipitate out in waters with a pH of 7.5 and above. Owing to the low solubility of many silver compounds (IJC 1977) and until further information is available, the level of 0.1 µg/L (0.0001 mg/L) total silver is recommended to provide protection for aquatic life.

It should be noted that in specific cases the current or even "natural" (predevelopment) concentration of silver in water might be higher than the recommended objective, since the average concentration of silver in surface waters was estimated to be 0.2 µg/L. In these as in all other cases, before an objective is recommended for a specific location, the local conditions, e.g., concentration, indigenous aquatic life, should be considered and the objective recommended here changed accordingly. It should also be noted that the detection limits for silver of the present routine analytical methods range from 4.0 to 10 µg/L, which are above that recommended for aquatic life. Therefore, the availability of analytical methods is another factor to be considered when recommending water quality objectives at specific locations.

Water Supply for Livestock

Silver in Animals

Silver is a general microconstituent of many land animals. The amounts of silver generally range between 1 and 10 mg/kg (in the ash). In beef meat it ranged from 0.001 to 0.025 mg/kg (wet weight) (Klein 1978f). Although the presence of silver in most animals suggests that it might serve some purpose, its role in animal metabolism is still unknown (Boyle 1968, p. 90). Silver entering an organism combines with plasma proteins from which it is removed by the liver and then eliminated in the bile through the gastrointestinal tract. More than 90% of the silver is eliminated, over 90% of it in the feces and very little in the urine. The silver that does not follow this pathway is deposited in the skin and mucous tissues (MRI 1975, p. 361; Cooper and Jolly 1970). Analysis of 32 milk samples from individual cows showed silver concentrations of 0.037 to 0.059 mg/L and an average concentration of 0.047 mg/L. The average silver content of milk from different cities in the United States varied between 0.027 and 0.054 mg/L (Murthy and Rhea 1968).

The Toxicity of Silver to Animals

Acute effects of silver in mammals are usually associated with intravenous administration, for example, silver nitrate has been used to produce acute pulmonary edema for study in dogs. Very little information is available in the literature about the effects of chronic exposure of silver in farm animals.

Studies quoted in the Midwest Research Institute report (MRI 1975, p. 359) suggested that silver salts in the diet of animals caused vascular hypertension. Rats given water containing 1000 mg Ag/L had their life span shortened and presented a higher incidence of hypertrophy of the left ventricle than a control group. Administration of drinking water containing 20 mg Ag/L to rats increased the DNA and RNA concentrations in the brain. After 12 months DNA and RNA levels were reduced and brain dystrophy was present. Rabbits administered 0.25 and 0.025 mg Ag/kg of body weight showed histopathological changes in the vascular, nervous, and glial tissues of the encephalon and medulla. Long-term experiments with rats and rabbits concluded that ingestion of silver in drinking water at a dose of 0.0025 mg/kg of body weight did not produce any detrimental effect. Doses of 0.025 mg/kg of body weight affected the rats' conditioned reflexes and rabbits' immunological activity (Barkov and El'piner 1968). Protargol, a silver protein containing 8% silver, inhibited the *in vitro* biosynthesis of prostaglandin by bull seminal vesicles (Deby *et al*. 1973).

A number of papers discussed the interactions of silver with other elements in animal nutrition. Data showed that silver was antagonistic to copper metabolism in chickens and cattle (MRI 1975, p. 359). In the absence of copper, 100 mg Ag/kg in the diet retarded the growth of chicks. Mortality of chicks receiving a copper-deficient diet was increased by levels of 50 mg Ag/kg or more, but in the presence of copper, silver had no effect (Hill *et al*. 1964). Silver and selenium were also antagonistic. Addition of silver acetate to the diet (130-1000 mg/kg) or drinking water (1500 mg/kg) of weanling rats fed a vitamin E-deficient diet led to liver lesions and a fatal liver necrosis after 2 weeks or more (Grasso *et al*. 1969). Results quoted in the same report showed that the addition of 0.05 or 0.1 mg Se/kg to the vitamin E-deficient diet was effective in preventing hepatic necrosis induced by the addition of 130 mg Ag/kg. At a level of 1000 mg Ag/kg, selenium was no longer capable of protecting against necrosis.

Recommended Objective for Water Supply for Livestock

There are not enough data published to give a definite assessment of the chronic toxicity of silver to farm animals.

The available information shows that silver has a low toxicity to higher forms of animals, it is eliminated rapidly especially when ingested orally and, unlike other metals (lead or mercury), it is not a cumulative poison (Cooper and Jolly 1970).

Neither the U.S. Environmental Protection Agency nor the Australian water quality criteria (Hart 1974) recommended any limit for silver in water supplies for livestock.

The surface waters in Canada contain very low concentrations of silver, and as there is not enough information available on the chronic toxicity of silver to animals, no limit has been recommended at this time for a silver concentration in water supplies for livestock.

Water for Irrigation

Silver in Plants and Soil

The concentration of silver in a series of "normal" well-drained New Brunswick podzol soils ranged between 0.1 and 7.8 mg/kg (Presant and Tupper 1965).

Silver tends to be retained in surface soil layers at pH greater than 4, especially in soils with a high concentration of organic matter, apparently owing to the strong adsorption of silver by humic colloids. Silver is also considered to bind to clay minerals, owing to the proximity of its ionic radius to those of sodium and potassium, and to a series of metal oxides such as MnO_2 (Klein 1978c). Data summarized by the same author show that when silver was added to the soil as a solution (concentrations of 0.5 and 5 mg/L as AgI), the concentration at the surface was approximately 10 times greater than the solution concentration, whereas at a depth of 5 cm they were about equal.

Silver, although widely distributed in nature, is not essential for plant life (Vanselow 1966) and silver is not a usual constituent of plants (MRI 1975, p. 362). Silver has the tendency to accumulate mainly in the root zone (Klein 1978d). The MRI report (1975, p. 50ff) and Vanselow (1966) summarized the available data on silver concentrations in plant tissues.

Ewing *et al*. (1969) determined the silver content in different fruits and vegetables and found a range of 0.02 to 0.1 mg/kg. An average content of 0.06 mg/kg has been given for land plants (Horovitz *et al*. 1974). In specific studies higher concentrations were measured, especially in fungi and mushrooms, although no plants have been found which regularly concentrate silver (Cooper and Jolly 1970). For example, Cooper and Jolly (1970) quoted silver concentrations in mushrooms as being "up to several hundred mg/kg dry weight." Horovitz *et al*. (1974) found a concentration of 16 mg/kg in *Clavulina cinerea* (a mushroom) and 10 mg/kg in *Caulerpa prolifera*. Some plants indicated a strong seasonal pattern with much higher levels of silver in May than September. *Ephedra gerardiana*, for example, contained 8 mg/kg in May and 0.02 mg/kg in September.

Other factors that influence the silver concentration in plants and the silver uptake by plants from soils are the plant species, the soil composition and its pH, and the silver form. Thus, for example, greenhouse studies have shown that silver from AgI is taken up to a much lesser extent than silver from $AgNO_3$ (Klein 1978d). The silver concentrations in tissues (roots, stems) of plants (sugar beet, Kentucky blue grass, corn) grown in $AgNO_3$-treated soil (26 mg Ag/kg) were greater by factors of 4 to 24 than concentrations in plants grown in AgI-treated soil (12 mg Ag/kg) (Teller and Klein 1973). On the other hand, no increase was observed in the silver concentration of maize, soybean and wheat grown in loam or sand soils enriched with 1000 mg Ag/kg (as AgI) compared with the plants grown on control soils (no silver enrichment) (An exception: wheat grown on enriched sand soil showed a 6-fold increase in its concentration). Similarly, no increase was observed in the silver concentration of maize grown on loamy or sandy soil enriched with 1000 mg Ag/kg (as $AgNO_3$) compared with maize grown in non-enriched soils (Weaver and Klarich 1973).

Results obtained by Vanselow and Bradford (Vanselow 1966) showed that silver did not accumulate in the leaves of citrus plants. The leaves of citrus plants grown in soil to which 75 mg Ag/kg had been added (as soluble silver nitrate) contained 0.5 mg Ag/kg. Boyle (1968, p. 85ff) quoted several references to the presence of silver in terrestrial plants, shrubs and trees. In general, the silver content in the ash is relatively low, usually of the order of 0.2 mg/kg. Higher values often occur in regions of silver mineralization, although in some cases there seemed to be no particular correlation between the amount of silver in a plant and the content of the element in its soil substrate. The ratio of silver content in plants to soil has been given as 1:1.5 (Lisk 1972). Such a ratio must be used with caution because the silver content of plants has a very wide range. For example, the silver content in the plants studied by Horovitz *et al*. (1979) had a span of 1600-fold.

The ratio of plant to soil silver concentration for grass from a subalpine meadow community went from a low of 0.06 (soil containing 127.1 mg Ag/kg, after treatment with $AgNO_3$ at a rate of 100 mg Ag/kg) to a high of 5.04 for grass from the control soils (0.028 mg Ag/kg) (Klein and Sokol 1976). Concentrations of 728 to 1015 mg Ag/kg (in ash) have been found in roots of experimental crops (corn, Kentucky bluegrass and sugar beet) grown on soils treated with $AgNO_3$ and containing 26 mg Ag/kg (dry weight). Thus, the ratio of silver concentration in root tissue to that in soil was 28 to 39. When the soil was treated with AgI and contained 12 mg Ag/kg (dry weight), the silver concentration in roots ranged from 43 to 176 mg/kg, i.e., a ratio of plant to soil of only approximately 4 to 15. In control soils (0.09 mg Ag/kg—dry weight) the roots' silver concentrations were 1.2 to 3.4 mg/kg (dry weight) giving a ratio of 13 to 38. Although the corresponding ratios for stems and leaves from the control crops were similar (range of 13 to 17), the ratios for the stems and leaves of crops from the treated soils were smaller, ranging from around 0.5 (AgI treatment) to 7 ($AgNO_3$ treatment). These results also confirmed the tendency of silver to concentrate in roots and the greater availability of silver from $AgNO_3$ compared with that from AgI or the "background" silver (Teller and Klein 1973).

Foliar applications of $AgNO_3$ solutions containing 150 mg Ag/L provided almost complete protection to pea seedlings from the growth retardation, stem swelling and horizontal growth produced by exogenously applied ethylene. The same protective effect by foliar application of $AgNO_3$ solution against ethylene effects was also observed with cotton, tomato and cucumber plants, and *Cattleya* orchids. No phytotoxicity was observed at the effective protective concentrations (Beyer 1976).

Toxicity of Silver to Plants

Laboratory studies reviewed briefly by Klein (1978c) have shown that silver, especially as silver ion, affected a series of soil microbiological processes, such as inhibition of soil maltase and urease, and produced changes in CO_2 evolution, microbial activity, population distribution of microorganisms and soil respiration processes.

Data concerning the toxicity of silver to terrestrial plants are scarce. Old data (1899) quoted by Cooper and Jolly (1970) showed a concentration of 9.8 mg Ag/L to be toxic to maize and 4.9 mg/L to lupines. Results quoted by Klein (1978d) show that neither wheat nor maize was significantly affected by concentrations of up to 460 mg Ag/kg of soil (as AgI) in either sand or loam. A concentration of approximately 640 mg Ag/kg of soil (as AgI) inhibited the germination of Engelmann spruce, whereas at lower levels a trend towards stimulation was observed. Slight damages to *Cattleya* orchids were observed when an $AgNO_3$ solution with a concentration of 9.5 mg Ag/L was applied directly to the flower (Beyer 1976). A decrease in the growth rate was observed for bean plants grown in nutrient solution containing 0.009 mg Ag/L (as $AgNO_3$).

There are some indications that concentrations of silver in soil or mud greater than 25 to 50 mg/kg may significantly alter the heterotrophic activities of the microorganisms in these environments (Sokol and Klein 1975).

A summary of the other available data can be found in the report by the Midwest Research Institute (MRI 1975, p. 380).

Recommended Objective for Silver in Irrigation Waters

The information available at present on the toxicity of silver to plants is inadequate to allow the recommendation of an objective for silver in irrigation water. Indications are that silver becomes toxic to plants at concentrations which are several orders of magnitude greater than those usually found in surface waters. Probably for the same reasons neither the U.S. Environmental Protection Agency nor the Australian water quality criteria (Hart 1974) include silver among the elements for which limits have been recommended for irrigation waters.

Recreation and Aesthetics

Drinking water supplies in recreational areas should comply with the level of 0.05 mg/L as total silver recommended for drinking water. It was not thought that levels of silver in sport fish would be a hazard to fish consumers; also a large proportion of the ingested silver is eliminated from the body.

The level recommended for aquatic life (0.0001 mg Ag/L) is much lower than that for drinking water, so waters where this level is applicable will be safe for sports involving body contact with water and water consumption.

Recommended Objective for Recreational Waters

The recommended objective for recreation is 0.05 mg/L as total silver.

Industrial Water Supplies

The food industry, where water is incorporated into the final product, is the only known industry where the level of silver in water is of concern. The level of silver in most Canadian waters is low and should not cause a problem elsewhere.

Water for the food industry should meet the same requirements as for drinking water.

Recommended Objective for Industrial Water Supplies

The level of 0.05 mg/L as total silver is recommended for industrial water supplies without treatment or with simple filtration. A level of 0.2 mg/L as total silver is recommended for water treated by chemical processes.

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